

Insulating Biomaterials N01-NS-2-2347

Fourth Quarterly Progress Report July-September, 2003

National Institutes of Health

National Institute of Neurological Disorders and Stroke

Neural Prosthesis Program



InnerSea Technology

**1 DeAngelo Drive
Bedford, MA 01730**

Contributors:

Dave Edell, PI

Bill Mather, IC Design

Robyn Edell, Testing

Sean Sexton, Instrumentation and Software

Ying-Ping Liu, Assembly and Testing

Karen Gleason, Chem Eng (MIT)

Shannan O'Shaughnessy, Grad Student, Chem Eng (MIT)



Objectives

The goal of the Insulating Biomaterials contract is to identify and evaluate materials, coatings, and assembly techniques suitable for protection of integrated circuit devices being considered for neural prosthetic applications. A lifetime design goal of 100 years of *in-vivo* functionality will provide a reasonable margin of safety for materials defined by this program. A multi-faceted research program is being pursued to allow investigation of known failure mechanisms of the materials and techniques under study as well as the discovery of new failure mechanisms. Both *in-vivo* and *in-vivo* testing will be used with a variety of testing procedures, devices, and materials to further discover, develop and understand insulating biomaterials for micro-machined devices.

Fourth Quarter Summary

New Instrumentation System

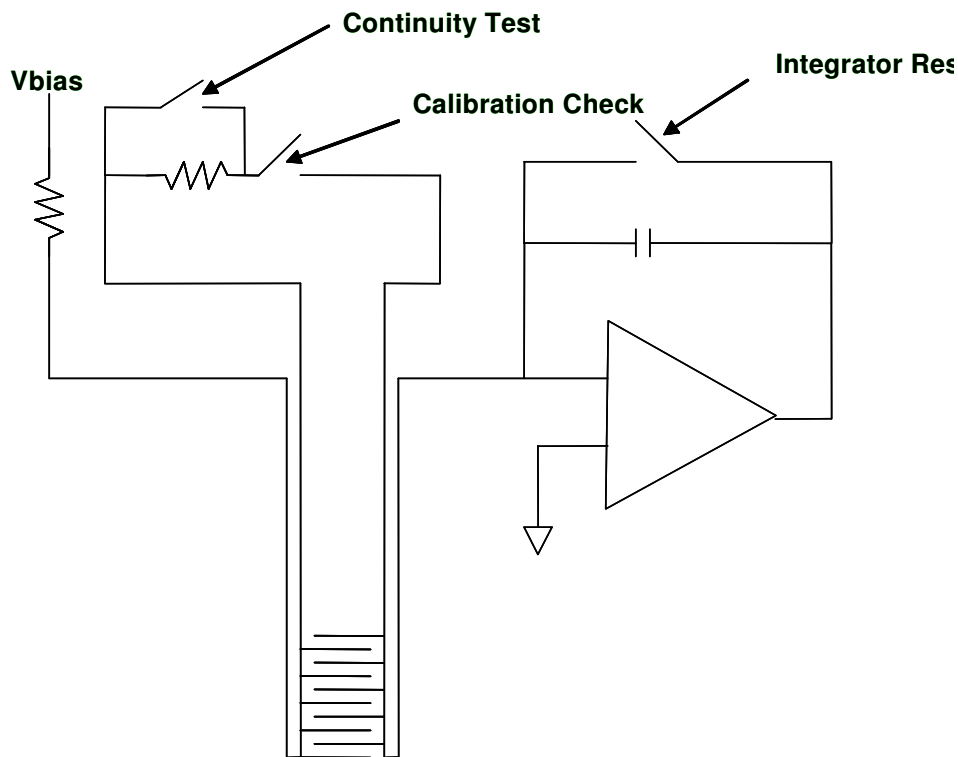


Figure 1: Continuity and calibration check added to integrator circuit.



The new instrumentation system design was revised to provide automated continuity and calibration checking (see sketch in **Figure 1**). System partitioning was also revised to reduce cost and complexity. In order to efficiently read out the individual units, a simple bus system will be implemented. While this will take some developmental time, once accomplished it will allow virtually unlimited additions to the system to take place without further modifications. In addition, it will save design and construction of a fairly massive multiplexing unit or the semi-bus structure previously considered. In our relatively lengthy experience with sensitive, automated test equipment, large multiplexing systems have been difficult to maintain, and prone to errors in setup as there is no absolute check of the channel assignments. Without such checks, it is possible for a multiplexer or software failure to result in recording data to the incorrect data set. While this can be determined during calibrations, it is difficult to catch, and intermittent failures are nearly impossible to detect unless obvious from the data itself.

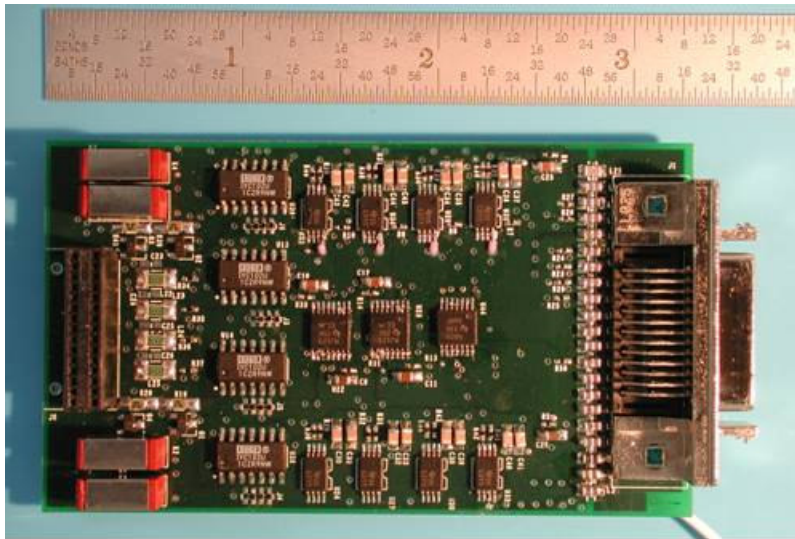


Figure 2: A 4 channel charge integrator for testing use of commercially available charge integrators for long term soak test measurement instrumentation.

A 4 channel charge integrator (Figure 2) based on commercially available devices was designed and fabricated in an effort to reduce the overall cost per channel for the long term soak test system. Results of testing indicate that the performance of the commercial devices in circuitry implemented on a multi-layer



printed circuit board technology is similar to that achieved by a full custom integrated circuit implementation, at a fraction of the cost. Example outputs are shown in **Figure 3**

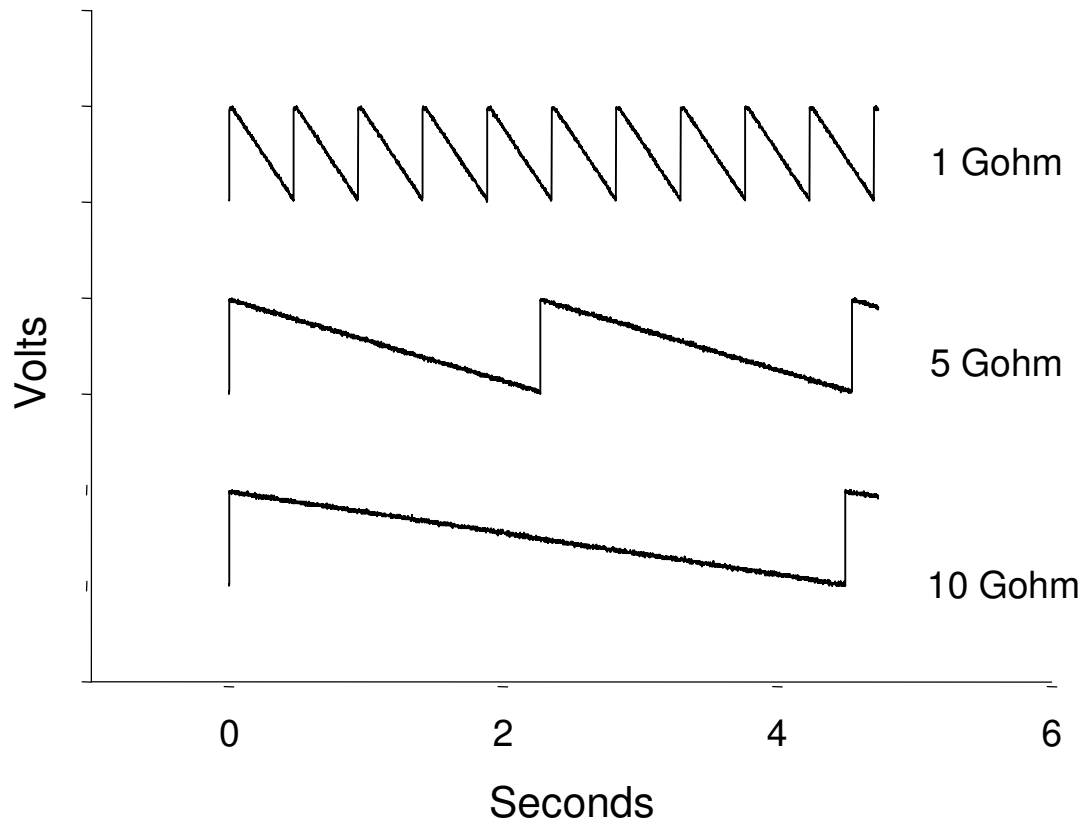


Figure 3: Example output waveforms from commercial device implementation of charge integrator. Note that the reset rate is inversely proportional to the magnitude of the resistance being measured.

Next quarter, the final approach will be selected based on overall cost estimates, and the final version of the system will be implemented.

Silicone Adhesion and Bonding

Additional testing targeted towards solving the issues of encapsulation of battery lead wires continued. Different commercially available adhesion promoters were studied for adhesion properties with the silicone wires. In all, six different versions of silane based adhesion promoters (Nusil) that were recommended for bonding silicones to silicones were tested. None provided strength greater than



the tear strength of the base silicone, indicating perhaps that active sites were shielded on the surface of the silicone by functional groups used to produce a “tight cure”. Another alternative could be that the chemistry of the wire insulation (GE860) is incompatible with platinum cure materials. This does not seem likely, as the material appears to have the physical properties from a normal cure.

The same commercial silane adhesion promoters were tested on quartz and glass slides. While long term testing has not yet been accomplished, initial pull testing was limited by the strength of the silicone as has often been the case with these samples. During re-examination of peel test devices that had exhibited variable peel forces and failure modes, to compare with those assembled with adhesion promoter, it became apparent that low peel forces was generally associated with failure of the bulk material. Initially, this relationship was missed because the failures appeared to be at the silicone-fiberglass interface. One such device was peeled under microscopic examination as part of the adhesion promoter testing. Surprisingly, there were micro-bubbles that expanded during the peel process to become visible (see **Figure 4**).

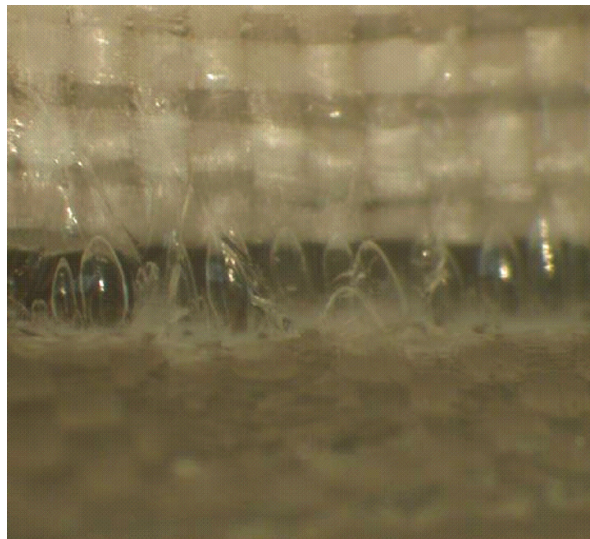


Figure 4 : Example of extreme case of micro-bubbles at the interface between fiberglass tape (top) and quartz substrate (bottom). Bubbles 50-100 μ m wide.

Variable numbers of micro-bubbles were observed at the peel interface. It may be that these bubbles can account for the variable peel forces and variable



failure modes previously observed. An obvious possibility is that the bubbles simply result in less dense silicone which will appear to have proportionally lower strength than a bubble free mixture. A variety of experiments revealed the consistent presence of microbubbles in the silicone-fiberglass preparation. With low viscosity silicones such as Nusil R2188, these bubbles can be eliminated by simply putting the preparation under vacuum prior to curing. However, with higher viscosity materials such as the MED4-4220, the normal cure is too rapid for the bubbles to dissipate under vacuum prior to cure. In addition, bubbles seemed to spontaneously develop during the cure process which could be enhanced by delaying the cure once the material was dispensed.

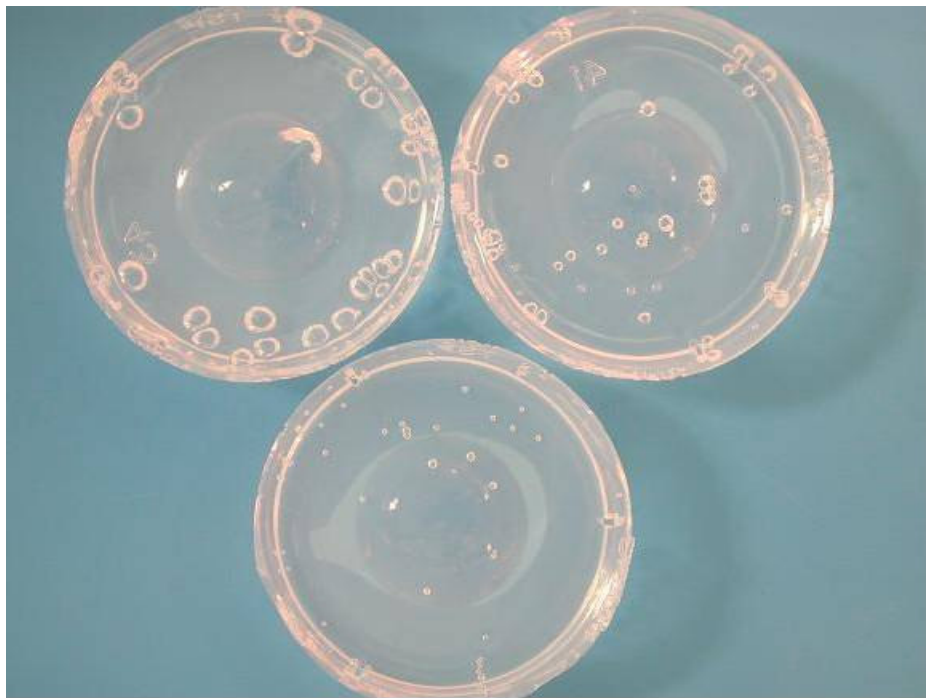


Figure 5: Example of spontaneous bubble formation during various time of pre-cure in three samples of Nusil MED4-4220.

Figure 5 shows results of a simple experiment where the silicone was dispensed directly into clean beakers and allowed to remain for varying lengths of time prior to curing. At room temperature, bubbles spontaneously formed in the samples and grew in size until the material was cured. In order to investigate this further, a custom formulation was designed in collaboration with Nusil, Inc. that will have



the same properties as MED4-4220, but which will have sufficiently long pot-life to allow vacuum de-gassing prior to curing. This material should be available next quarter.

CVD Synthesis of New Materials

Removing Flaws from Films

Previous attempts to deposit co-polymeric films utilizing Trivinyl-TriMethyl-Cyclotrisiloxane (V_3D_3) and Perfluorooctane-sulfanyl fluoride (PFOSF) as precursors have resulted in coatings possessing numerous flaws and inclusions. These flaws, visible under optical microscopy, vary in size from 50-200nm. In order to proceed to the desired next step of creating resistive wire coatings from this chemistry, it is necessary to determine the nature of these flaws and eliminate them from the films.

The films containing flaws were created utilizing hot filament CVD with a Nichrome (85% Nickel, 15% Chromium) filament wire. Filament temperature for deposition ranged between 370-540°C. Additionally, the films were produced in the Gleason Lab's "Death Star" reactor which contains a large gas recirculation cell.

Previous experience showed that very thin (<1µm), nearly flaw free, films could be created in the Gleason Lab's "Charlotte" reactor in which flow is fairly uniformly one dimensional. These depositions also utilized a Constantan (45% Nickel, 55% Copper) filament wire. However, deposition rates were very limited in the Charlotte reactor (most likely due to low gas residence times), and some flaws still existed. The relative lack of flaws in the Charlotte films posed the possibility that the flaws in the Death Star films were due to inclusion of metal particles, most likely Chromium.

In order to determine the source of the flaws, the previous process conditions were replicated, with the resulting films matching quite well with prior experience (i.e., a highly flawed thick film from Death Star and a slightly flawed thin film from Charlotte). These films were then examined utilizing an ESEM with an EDAX



attachment to determine the chemical composition of the flaws. However, under ESEM, no particulate was visible. Indeed, the only chemical elements present (determined by EDAX) were those in the precursors or the substrate. Further examination of the samples revealed that the inclusions were not particulate but pinholes or holidays in the film.

Additional samples were prepared in Death Star utilizing a Constantan filament wire. These depositions resulted in thick, flaw free films. Holidays were not visible under either optical microscopy or ESEM examination. While the precise cause of the holidays in the previous Death star films is still unknown, it is theorized that the Chromium in the Nichrome filament catalyzes rapid gas phase growth creating large particles which do not fit neatly together when deposited on the substrate. Additionally, it is also possible that some Chromium (though at levels below what was detectable by the instruments used) is included in the films. Despite this uncertainty, it is now possible to produce thick, flaw free co-polymeric films.

Wire Coating Progress

The success in removing flaws from the co-polymer films deposited on silicon substrates suggested that it may be possible to produce flaw free wire coatings as well. To test this, coatings were produced on 50um platinum wire in the Death Star reactor utilizing a Constantan filament at 550°C. Reactor pressure was held at 350mtorr, and the precursor ratio was 2:1 V_3D_3 to PFOSF. Deposition of ~8um was observed on a silicon wafer placed below the wire. Flaw free coatings were observed on the wire under optical microscopy, though the wire coatings did not appear to be as thick as the coating deposited on the wafer. It is estimated that the wire coating was only ~2-3um. However, despite the flaw free nature of the coating, the film was not flexible and exhibited substantial cracking when the wire was flexed or knotted. This cracking, which prevented accurate testing of the wire coating resistivity, is obviously not allowable for the proposed application.



The source of the coating inflexibility is readily found from previous work with wire coatings produced using a Nichrome reactor filament. At high filament temperatures, ring opening reactions of the V_3D_3 precursor create highly cross-linked structures which are rigid in nature. The lower the temperature of the filament, the less cross-linking occurs, and the more flexible the film is.

Unfortunately, the Constantan filament wire is unable to significantly decompose the PFOSF initiating precursor much below $500^{\circ}C$. The difference between this and the Nichrome wire, which could decompose PFOSF down to $\sim 350^{\circ}C$, is assumed to be the lack of catalytic Chromium in the Constantan filament.

However, as the presence of Chromium in the filament leads to flaws in the film, Chromium catalysis can not be used to reduce the filament temperature.

Therefore, another method of creating more film flexibility must be found.

To this end, additional wire coatings with a 1:1 V_3D_3 to PFOSF precursor ratio were produced in the hope that the addition of more CF_2 units, which can not crosslink, in the film composition would prevent the film from becoming inflexible. Optical microscopy of these coatings showed flaw free films which exhibited significantly less cracking when the wire was flexed or knotted. However, some cracking was still present and prevented measurement of coating resistivity.

It is theorized that a coating which is primarily fluorocarbon in nature, with only small amounts of organosilicon to prevent crystallization, would be flexible enough to withstand required manipulation of the wire. Work in the immediate future will focus in this area, with experiments testing both higher PFOSF to V_3D_3 ratios as well as the addition of HFPO as a third precursor to provide even higher CF_2 content in the coating.